Investigation of Iron Dissolution Mechanism in Acidic Solutions with and without Dissolved CO₂—Part II: Time of Flight-Secondary Ion Mass Spectrometry 3D Mapping

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Time-of-flight-secondary ion mass spectrometry (ToF-SIMS) 3D mapping and depth profiling were used to study the anodic iron dissolution mechanisms of mild steel in chloride-containing aqueous CO_2 environments. The technique detected adsorbed hydroxide and chloride intermediates formed during the corrosion process, consistent with the proposed multipath reaction mechanism for anodic iron dissolution reaction. Despite the presence of aqueous carbonic species and their observed effect on the kinetics of iron dissolution, no additional adsorbed intermediates have been detected in aqueous CO_2 environments, indicating that carbonic species do not directly participate in the iron dissolution reaction. ToF-SIMS 3D mapping results on characterization of the specimens immersed in a chloride-containing solution with and without CO_2 suggest that one role of aqueous carbonic species CO_2 could be to accelerate the adsorption of chloride ions and the formation of chloride intermediates.

KEY WORDS: anodic iron dissolution mechanism, chloride, CO2 corrosion, hydroxide, mild steel, time of flight-secondary ion mass spectroscopy

INTRODUCTION

nternal corrosion of operating pipe flow lines made from mild steel is a very common type of corrosion in the oil and gas transportation industry,¹ especially the so-called "sweet" corrosion (i.e., corrosion due to aqueous CO_2). Aqueous CO_2 corrosion of mild steel often results in a higher corrosion rate than that observed in strong acid solutions with the same pH. The role that aqueous CO_2 and its hydration product: carbonic acid (H₂CO₃) play in acidic corrosion is rather complex.

The relevant mechanistic understanding of CO₂ corrosion of mild steel has evolved over the last 50 y, mostly focused on the cathodic reactions. The two most well-known mechanisms for the role of H₂CO₃ in cathodic reaction sequence were: the "direct reduction mechanism" and "buffering effect mechanism." Direct reduction of H₂CO₃ has been considered the main cathodic reaction in CO₂ aqueous solutions since the mid-1970s.² More recently, several modeling studies indicated the significance of homogeneous H₂CO₃ dissociation and put forward the "buffering" effect, which considered H₂CO₃ as nonelectroactive species and its main role to provide H⁺ by homogenous dissociation to "feed" the hydrogen evolution reaction.³⁻⁵ Due to the experimental limitations, this buffering effect gained little attention until recently Tran, et al.,⁶ and Kahyarian, et al.,⁷⁻⁹ created the necessary experimental conditions for directly investigating the mechanism of the H₂CO₃ reduction. Kahyarian, et al.,⁷⁻⁹ achieved this by setting CO₂ partial pressure up to 5 bar and designing an innovative thin channel flow cell setup that allowed high flow and therefore increased the limiting current so that the charge transfer current could be observed clearly within an extended range of potentials. Their results showed that the direct reduction of H₂CO₃ is negligible and the buffering effect is the main cathodic reaction mechanism.

As for the role of CO_2 in anodic iron dissolution reaction in an acidic solution, the relevant mechanistic studies are not as extensive as the studies related to CO_2 effect on cathodic reactions. In some studies, it has been demonstrated that there is a significant effect of CO_2 on the anodic iron dissolution reaction.¹⁰⁻¹² We can start here by briefly reviewing the kinetics and mechanisms of iron dissolution reactions, leaning on a more detailed literature review provided in Part I of this article series. Part I is in preparation process.¹³

For strong acids, there are three classic iron dissolution mechanisms: the "consecutive mechanism" by Bockris, et al.,¹⁴ the "catalytic mechanism" by Heusler,¹⁵ and Keddam, et al.,

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multi-path scheme.¹⁶⁻¹⁷ In all three cases, a significant role is assigned to adsorbed OH⁻ ions that form complex intermediates at the surface, directly involved in the iron dissolution mechanism. The "consecutive mechanism" was based on the 40 mV experimental Tafel slope and first-order dependence on OH⁻ concentration observed by Bockris, et al.¹⁴ The "catalytic mechanism" was derived based on the observed Tafel slope of 30 mV and second-order dependence on OH⁻ concentration, according to Heusler.¹⁵ The observed differences in kinetics in these two classical studies were caused by the different surface activities of the iron electrode.¹⁸⁻¹ However, the iron dissolution reaction is more complex than these two mechanisms accounted for, as in acidic solutions it can occur differently in different potential ranges: close to the open-circuit potential (OCP) we have active dissolution, then at more positive potentials-transition, prepassivation, and finally passivation.²⁰ Both the catalytic and the consecutive mechanisms are associated with the electrochemical behavior observed in the active dissolution range near the OCP. Keddam, et al.,¹⁶⁻¹⁷ proposed a more comprehensive mechanism, including multiple parallel dissolution paths for iron dissolution, involving both the consecutive and the catalytic mechanisms and covering a broader potential range.

However, all of these landmark studies were conducted in strong acid solutions containing sulfates, hence the role of chlorides which is almost always present in CO₂ containing brines was not covered. While there is plenty of controversy on the exact role of chloride in iron dissolution in acidic solutions, there is also some agreement that Cl⁻ ions might partially displace adsorbed OH⁻ at the iron surface through competitive adsorption and thereby affect iron dissolution. In such scenarios, some studies indicate that halides such as Cl⁻ can decelerate the anodic reaction while other studies report an acceleration effect of Cl⁻ on the anodic dissolution of iron. Several important studies on this subject are reviewed in Part I of the present article series, including the Kuo and Nobe²¹ consecutive mechanism, and the MacFarlane and Smedley²² proposal based on Keddam's multipath scheme. Finally, an alternative mechanism is proposed based on electrochemical impedance spectroscopy (EIS) characterization of iron dissolution in sulfate and chloride solutions, which also builds on Keddam's multipath mechanism.

When it comes to CO₂ corrosion and iron dissolution in weak acid solutions, the anodic polarization curves in the active dissolution domain, close to OCP, have been reported to have a 40 mV Tafel slope and a first-order dependence on OH⁻ concentration. Therefore, the "consecutive mechanism" of Bockris, et al.,¹⁴ for strong acids has been usually adopted to describe the iron dissolution reactions and kinetics in CO₂ corrosion while any effect of dissolved CO₂ was neglected. Linter and Burstein¹¹ reported that CO₂ significantly increased the iron dissolution rate of 0.5 Cr alloyed steel in the transition and prepassivation range, while the active dissolution range was not influenced. Kahyarian, et al.,¹² reported that in the transition and prepassivation ranges, the anodic reaction rate of mild steel has a significant dependence on the partial pressure of CO₂, which is consistent with Linter and Burstein's findings. Kahyarian, et al.,¹² also pointed out that in the anodic dissolution range, the presence of CO₂ decreased the Tafel slope (increased reaction rate) when the partial pressure of CO_2 (pCO₂) is as low as 1 bar and this effect was not intensified with a further

increase of pCO₂. This observation for the active dissolution range agreed with Nešić, et al.,¹⁰'s study covering a relatively narrow potential range above the corrosion potential where the effect of CO₂ was found to reach its maximum as pCO₂ approaches 1 bar. Based on these electrochemical observations about the CO₂ influence on the iron dissolution reaction, there were some hypothetical explanations put forward, suggesting the role that carbonate species adsorbed on the metal surface play, when they interact with iron hydroxide and iron chloride intermediates leading to an increase in the rate of the anodic iron dissolution and increase of the corrosion current. However, Almeida, et al.,'s EIS results indicated that CO₂ does not react directly with the iron surface at OCP under their experimental conditions,²³ which is a different conclusion compared to the other studies listed above. The EIS study reported in Part I of this paper series,¹³ agreed with the conclusions drawn by Almeida, et al.²³ In summary, so far there are only a few plausible hypotheses about the role of CO₂ in anodic dissolution of iron, based on scattered electrochemical observations, with some of them contradicting each other.

All of the previously listed investigations of the mechanisms of CO₂ corrosion were done by using electrochemical techniques, most of them steady state, except for Almeida, et al.,²³ and the one reported in Part I of the paper series. In all of them, the existence of various intermediate species was postulated without direct evidence, making the associated iron dissolution mechanisms speculative. In the past, traditional scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS), and x-ray diffraction (XRD) analyses have been extensively used in CO2 corrosion studies. However, they all have a limited sensitivity for detecting the reaction intermediates during the anodic dissolution of iron needed to help clarify the mechanisms. High-resolution transmission electron microscopy (TEM) was sometimes used to look at the macroscopic iron carbonate corrosion product layer structure and composition, which formed in long-term exposure of steel in CO₂ aqueous solutions. However, the mechanism of iron dissolution and the intermediates that form during the initial corrosion stages of the bare steel surface were not investigated in these studies.²⁴⁻²⁵

The work presented below is the second part of a two-part article, where the EIS analysis presented in Part I is complemented with time-of-flight-secondary ion mass spectrometry (ToF-SIMS) results, used to study the anodic iron dissolution mechanisms in CO_2 corrosion. ToF-SIMS in-depth profiling and 3D mapping were used on mild steel corroding in aqueous CO_2 solutions to directly detect the intermediate compounds that form, covering a broad range of conditions. This information was used to examine the validity of the proposed mechanisms of iron dissolution that were based solely on electrochemical measurements.

EXPERIMENTAL PROCEDURE

2.1 | Sample Preparation

UNS G1018 (UNS G10180⁽¹⁾) steel samples, which consist of 0.018% C, 0.75% Mn, 0.011% P, 0.021% S, and 0.0067% N and Fe in balance, were cut out in a form of a 1 mm to 3 mm thick flat square sheet with 1 cm × 1 cm area. These mild steel samples were sequentially ground using 600, 1200, 2400, and 4000 SiC papers under water flow, and then polished down to 0.25 μ m with alumina oxide suspensions. The polished samples were finally thoroughly rinsed with distilled water and quickly dried under a stream of compressed air.

⁽¹⁾ UNS numbers are listed in *Metals & Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE International) and cosponsored by ASTM International.

2.2 | Immersion Tests

The 1 wt% NaCl solutions saturated with CO₂ or Ar were used as a corrosive medium. The solutions were prepared using deionized water with a conductivity of 18 M Ω ·cm⁻¹. Before sample immersion, the solution was purged by CO₂ gas or neutral Ar gas bubbling for at least 2 h to remove dissolved oxygen and saturate the solution. The initial pH of the test solution was 3.9±0.1. For Ar saturated NaCl solution, to keep the initial pH 3.9 value (the same as obtained spontaneously in a CO₂ saturated NaCl solution), 1 M HCl was used to adjust the solution pH value (the added amount of extra chloride ions is very small and has negligible effect). The pH drift was monitored during immersion test and kept within 0.1.

Immersion tests were carried out in 50 mL glass vials at room temperature (25±2°C). Gas bubbling was continuously maintained during the sample immersion. The immersion times were set as 3 min, 10 min, and 1 h. After the denoted immersion time, the sample was taken out, rinsed with distilled water, dried in a stream of Ar gas, and immediately transferred to the ToF-SIMS spectrometer where it was analyzed. The composition and structure of the analyzed oxide layer on the specimen is thought to be rather stable during the short time it took to transfer the specimen, due to a protective Ar gas atmosphere that was maintained at all times.

2.3 | Time-of-Flight-Secondary Ion Mass Spectrometry Characterization

ToF-SIMS measurements were performed using a dual beam ToF-SIMS V spectrometer (IONTOF[†] GmbH, Muenster, Germany). The base pressure in the analysis chamber is maintained at less than 5.0×10^{-9} mbar in normal operating conditions. The total primary ion flux was less than 10^{12} ions cm⁻² to ensure static conditions. Depth profile measurements were performed in high-current bunched mode (IONTOF GmbH property name, with mass resolution [M/ΔM] around 3,000) with a dual beam using a pulsed 25 keV Bi⁺ primary ion source delivering 1.2 pA of target current over a 100 µm × 100 µm area (45° incidence to the specimen surface) interlaced with a 500 eV Cs⁺ sputter beam delivering 25 nA of target current over a 300 µm × 300 µm area (45° incidence to the specimen surface). Negative ions in-depth profiles were recorded, as they provide a better sensitivity for oxide species.

For measurements of 3D images, the spectrometer was run in BA-Image mode (IONTOF GmbH property name) with 512 by 512 pixels, 4 shots/pixel which gives good lateral resolution (about 200 nm), with lower mass resolution (M/ΔM around 100). There was no overlapping of peaks in the mass range considered to plot the 3D images or, at least, if a slight overlapping of peaks occurs, the masses of interest are the most intense in the mass ranges considered to plot 3D images. 3D image measurements were performed in dual beam mode using a pulsed 25 keV Bi⁺ burst primary ion source delivering 0.2 pA of target current over a 100 µm × 100 µm area interlaced with a 500 eV Cs⁺ sputter beam delivering 25 nA of target current over a 300 µm × 300 µm area (45° incidence to the specimen surface), and the negatively charged ions were recorded. As ToF-SIMS is not a quantitative technique (due to the strong matrix effect on ion emission), the intensity of the plotted ions cannot be compared directly and does not reflect the concentrations of the associated species in the substrate.

RESULTS AND DISCUSSION

3.1 | Time-of-Flight-Secondary Ion Mass Spectrometry Analysis of Iron Dissolution Mechanisms in Acidic Aqueous Solutions

ToF-SIMS depth profiles and 3D images were used to study the structure of the oxide film formed on 1018 mild steel before and after immersion in a CO₂ saturated 1 wt% NaCl solution, for 3 min, 10 min, and 1 h. The detected Fe⁻₂ signal is characteristic of the metallic substrate and the beginning of the intensity plateau is used to localize the metal/oxide interface.²⁶ The FeO⁻₂ and FeO₂H⁻ signals indicate adsorbed iron oxide and hydroxide iron. The Cl⁻ and FeOCl⁻ signals are used to indicate the adsorbed chloride ions and iron chloride intermediates. The ³⁷Cl⁻ species was used in the depth profiles to remove the possible saturation of chloride species in HC-Bunched mode due to the very high ionization yield of chloride in negative polarity. The ³⁵Cl⁻ species was used in the BA image mode and no saturation of the signal occurred.

The ToF-SIMS in-depth profile of the native layer formed in air on 1018 mild steel is shown in Figure 1(a). This gives a reference for the comparison with in-depth profiles recorded after immersion in the NaCl solution saturated with CO_2 for various immersion times, which can reveal the effect of anions (OH⁻ and Cl⁻) on the structure, composition, and thickness of the surface layer, thereby shed a light on the iron dissolution reaction mechanism in CO_2 corrosion.

For the native surface, the FeO₂ depth profile shows an intense signal over the first 50 s of sputtering time, while the intensity of FeO₂H⁻ and FeOCl⁻ signals (characteristic of iron hydroxide and iron chloride species, respectively) remain very low, indicating that the native layer is mainly composed of iron oxide. After probing deeper into the substrate (i.e., longer sputtering time), the decrease of the oxidized species, concomitantly with the increase of the Fe₂ signal around 50 s of sputtering, indicates that the metallic substrate is reached. The structure and composition of the oxide scale is confirmed by the 3D images (Figures 1[a1] through [a6]). Before immersion in NaCl-containing solution, a Cl⁻ signal is observed during the first seconds of sputtering. The Cl⁻ signal is assigned to chloride contamination of the surface during surface preparation. The quite high intensity of the Cl⁻ signal results from the very high ionization yield of CI in negative polarity.

Figures 1(b) through (d) show the ToF-SIMS depth profiles obtained on mild steel after different immersion times in CO₂ saturated NaCl aqueous solution. As immersion time in CO₂ saturated NaCl solution increases, the drop of FeO₂⁻ signal becomes less sharp, which indicates the roughening of the Fe oxide/metal substrate which is caused by continuous corrosion. The roughening of the metal/oxide interface is confirmed by the trend of the increase of the Fe₂ signal in the interfacial region that shows a slower rise when increasing the immersion time in the CO_2 saturated chloride solution. Looking at the Cl⁻ and FeOCl⁻ signals, one observes, as soon as the substrate is immersed in the CO₂ saturated chloride solution, a huge increase of their intensities on the surface and in the oxide scale. Moreover, their intensities increase with increasing immersion time from 3 min to 1 h. This indicates that the oxide/hydroxide layer formed on the mild steel substrate contains chloride, which is a result of specific adsorption of chloride ions, followed by the formation of chloride-containing intermediate complexes (oxychloride species) on the iron substrate. Further study of the FeO₂H⁻

[†] Trade name.



FIGURE 1. ToF-SIMS negative ions in-depth profiles and 3D images for 1018 mild steel before and after immersion in 1 wt% NaCl solution saturated with CO_2 for different immersion times. Depth profiles: (a) native oxide layer before immersion, (b) 3 min, (c) 10 min, and (d) 1 h immersion; 3D images: five species and their overlay (a1-a6) before immersion, (b1-b6) 3 min, (c1-c6) 10 min, and (d1-d6) 1 h immersion.

signal gives even more information. In fact, as for FeOCI⁻, the intensity of the FeO₂H⁻ signal drastically increases with exposure time to CO₂ saturated chloride solution. Initially maximum in the outer oxide (peak observed at 10 s of sputtering for 3 min), the maximum intensity of FeO₂H⁻ progressively spread through the oxide scale to entirely dominate it after 1 h of immersion. Thus, upon immersion in chloride-containing aqueous solution, both iron hydroxide and iron chloride intermediates are quickly formed, first located on the oxide surface, and then distributed throughout the entire thickness of the layer. Thus, the layer after 1 h intermediates.

The 3D images of FeO_2H^- (Figures 1[a3] through [d3]) confirm the immediate formation of iron hydroxide intermediates in the top surface layer for short-immersion times, and then the progressive distribution throughout the whole surface layer until deeper substrate region for longer immersion times at 1 h. The 3D images of FeOCl⁻ (Figures 1[a4] through [d4]) show that

the distribution of iron chloride intermediates is more localized, especially in the initial stages at 3 min and 10 min immersion. After 1 h immersion, although the iron chloride intermediates are still enriched in some localized patches, they already spread through the whole space from the surface layer to substrate. This indicates potential "pits" may form to initiate corrosion at shorter immersion time, and then gradually develop into general corrosion with longer immersion times. After 1 h, the whole surface is corroded and becomes very rough as indicated by the 3D images of Fe₂ signal. This work is limited to 1 wt% NaCl, and it will be very interesting to investigate with ToF-SIMS what would happen at higher salt concentrations: whether there would be a decrease of general corrosion rate as indicated by electrochemical measurement, or if pitting would be initiated.

As shown by the overlayed 3D images from Figures 1(a6) through (d6), before immersion, the native oxide consists of a thin iron oxide layer covering the substrate, with a sharp metal/



oxide interface. After 3 min and 10 min immersion times in CO_2 saturated chloride aqueous solution, the modification of the surface layer composition (formation of a mixed surface layer with iron oxide, iron hydroxide, and iron chloride intermediates), as already discussed above, is accompanied by the roughening of the metal/oxide interface, as already stated from the depth profiles.

Let us now consider how these findings can be linked to the iron dissolution mechanisms mentioned above, discussed in more detail in Part I of this article series. The observed change of surface layer compositions can be readily associated with parallel reaction paths involving the participation of hydroxide ions and chloride ions in the anodic iron dissolution reaction happening in acidic solutions.^{22,27} The overall reaction for the anodic dissolution of iron is

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^{-}$$
⁽¹⁾

but the actual reaction path (mechanism) for this two-electron oxidation reaction is more complex. The foundation of the explanation used here is the multipath mechanisms originally proposed by Keddam, et al.,¹⁶⁻¹⁷ for strongly acidic sulfate

solutions. As a reminder, it includes Path no.1 which is similar to Bockris's consecutive mechanism,¹⁴ and Path no. 2 which follows the Heusler's catalytic mechanism,¹⁵ both involving the adsorbed hydroxide ions forming intermediate species with iron. These two mechanisms were proposed based on experimental data obtained near the OCP. Path no. 3 is related to prepassivation and passivation at more positive potentials and is not relevant in the present discussion, which is focused on the measurements and mechanisms that prevail closer to the OCP.

As described in Part I of this article series, ¹³ these three parallel iron dissolution mechanisms, include three adsorbed intermediate complexes: $FeOH_{(ads)}$, $Fe(FeOH)_{(ads)}$, and $Fe(Fe(OH)_2)_{(ads)}$. The latter two complexes are catalytic intermediates formed by the transformation of adsorbed $FeOH_{(ads)}$ on the surface of Fe, in Path no. 1 and Path no. 2 of Keddam's multipath mechanism, respectively. It is worth pointing out that, even with a high-resolution analytical technique, such as the one deployed in this study, the exact composition of these adsorbed intermediate compounds cannot be fully determined, but their existence and distribution can be confirmed. Hence, we can conclude that one clear possibility is that the increased levels of FeO_2H^- detected in the ToF-SIMS depth profiles are associated with the formation of $FeOH_{(ads)}$ and/or $Fe(FeOH)_{(ads)}$ adsorbed intermediates during the iron dissolution reaction.

Following Moradighadi, et al., in Part I of the article series which used EIS to investigate the mechanism of iron dissolution at OCP.¹³ we have proposed in Part I of this article series an additional parallel Path no. 4 for the dissolution of iron that involves adsorbed chloride intermediate $Fe(FeCIOH)^{-}_{(ads)'}$, which is consistent with some suggestions from previous studies.²¹⁻²² Therefore, the FeOCI⁻ peak detected in the ToF-SIMS depth profile is likely associated with this adsorbed chloride intermediate or oxychloride species.

In summary, the evolution of composition observed in the ToF-SIMS depth profiles and 3D images, changing from being mainly iron oxide in the native layer to a mixture of iron oxide, hydroxide, and chloride adsorbed intermediates after exposure, shown in Figures 1(a6) through (d6), provide a strong argument in support of the parallel pathways for iron oxidation involving adsorbed OH⁻and Cl⁻ ions, presented in Part I of the article series.

It should be pointed out at this point, that even if experiments were conducted in an aqueous solution saturated with CO₂, very low traces of carbonic species were detected in the ToF-SIMS depth profiles. ToF-SIMS depth profiles of the FeCO₂ species for the native layer and for immersion times of 3 min, 10 min, and 1 h are plotted in Figure 1. First, the drop of the FeCO₂ signal becomes less sharp with increasing immersion times, confirming the roughening of the Fe metal/oxide interface caused by iron dissolution. Second, the intensity of the FeCO₂ peak at around 30 s does not change for different immersion times by comparison with the native layer. Compared with the significant peak intensity changes of FeO₂H⁻, FeOCl⁻, and Cl⁻ before and after immersion, it can be concluded that CO₂ does not influence the anodic iron dissolution reaction in the same way as hydroxyl ions and chloride ions do. In addition, the intensity of FeCO₂ in the substrate plateau region is similar to that of FeO₂H⁻ and FeOCl⁻ in the native layer but it becomes much less than that of FeO_2H^- and $FeOCI^-$ after immersion. The fact that the intensity peak of FeCO₂ does not change indicates that no extra iron carbonate complexes are formed in CO2 saturated solutions and that there is no direct reaction between carbonic species and iron. This is consistent with the findings of Moradighadi, et al., in Part I of the article series and Almeida, et al.,²³ showing that the presence of aqueous CO₂ does not result in the formation of new adsorbed intermediate complexes, and the conclusions reached in Part I of this article appear to hold.

To further understand the nature, composition, and structure of surface layers formed on the mild steel in CO2saturated NaCl solution, 2D ToF-SIMS images, reconstructed from the ToF-SIMS 3D analyses on the specimens immersed in NaCl solution for different immersion times, are built and shown in Figure 2. Cl⁻, FeO₂, FeO₂H⁻, and FeOCl⁻ images correspond to 2D plots integrating images from the whole oxide film region (the integration range, i.e., the depth of the whole oxide film for each immersion time, is taken from the corresponding depth profile [Figure 1], corresponding to the first 50 s, 50 s, 60 s, and 80 s of sputtering time for 0 min, 3 min, 10 min, and 1 h immersion, respectively). The bright yellow colors shown in ToF-SIMS 3D top view mapping indicate the enrichment of selected ions, while dark black indicates the absence of selected ions. Although characteristic of the metallic substrate underneath the oxide film, Fe₂, and CFe⁻ (characteristic of iron carbides) is also reconstructed.

The Cl⁻ chemical maps (Figures 2[a1] through [d1]) evidence that no Cl⁻ ions are found in the oxide/hydroxide layer covering the mild steel before immersion in CO_2 saturated chloride solution (Figure 2[a1]). With increasing immersion time, the chloride ions progressively spread throughout the whole oxide/hydroxide layer, as shown in the images after 1 h of immersion (Figure 2[d1]). The dendritic shape in the oxide/ hydroxide layer observed after 3 min and 10 min of immersion (Figures 2[b1] and [c1]) suggests that the chloride species are mainly the result of the formation of chloride-containing iron complexes on the steel surface. This is in accordance with previous conclusions made from ToF-SIMS depth profiles.

For the 3D top view mappings of FeO₂ and FeO₂H⁻ ions, a homogeneous distribution of iron oxide and iron hydroxide is observed in the native layer, as shown in Figures 2(a2) and (a3). After immersion in the NaCl solution, there is a development of several "defects" in that layer that correspond to the lowintensity regions in the FeO_2^- and FeO_2H^- images (dark areas in Figures 2[b2] through [d2] and 2[b3] through [d3]). The size and density of the defects both seem to increase with increasing immersion time in CO2-saturated chloride solution. Interestingly, these defects also correspond to regions where an intense FeOCI⁻ is detected in the maps (bright areas in Figures 2[b4] through [d4]). This indicates that intermediate chloride complexes (oxychloride species) formed in clusters and propagated upon immersion. Moreover, at locations where iron chlorides are found, there were no iron hydroxides and vice versa. This observation can be associated with the "competitive adsorption" process between chloride ions and hydroxyl ions as well as the formation of corresponding iron complexes. It is known that halides, including chloride ions, have strong specific adsorption and compete for sites on steel surfaces with other species such as hydroxyl ions.²⁷⁻³⁰ For iron, Lorenz,³¹ brought out the concept of "competitive adsorption" between chloride ions and hydroxyl ions

$$OH_{ads}^{-} + CI^{-} \xrightarrow[diluted]{Concentrated} CI_{ads}^{-} + OH^{-}$$
 (2)

They suggested that the hydroxyl ions in "catalytic mechanism"¹⁵ can be replaced by chloride ions and that chloride ions participate in the formation of the intermediate complex. McCafferty and Hackerman³² as well as Kuo and Nobe^{21,33} modified the Lorenz model to further emphasize the competitive adsorption of hydroxyl ions and chloride ions in the electrochemical mechanism for iron dissolution. Moradighadi, et al., recast this in the form of the fourth pathway added to the Keddam, et al., scheme, as shown in Part I of this article series.¹³ It can therefore be argued that the detected FeOCI⁻ signal in 3D top view mapping comes from the formation of the catalytic chloridecontaining intermediate (actually an oxychloride species). The fact that this intermediate is exactly at the location of the defects in accumulated hydroxide intermediates, provided direct visual evidence for the "competition" between chloride ions and hydroxyl ions, as well as their parallel reactions with iron.

The steel substrate, characterized by the Fe_2^- signal, also shows deficiencies in Figures 2(b5) through (d5), coincides with the location of enrichment in iron chloride intermediates characterized by the FeOCI⁻ signal, confirming the finding from 3D images that the potential "pits" formed in the metallic substrate and filled with iron chloride/oxychloride intermediates As immersion time increases, the intensity contrast between these "pits" and surrounding metal surface gradually decreased, indicating gradual development into more general corrosion.

SCIENCE SECTION



FIGURE 2. ToF-SIMS 3D top views chemical maps of (a1-d1) Cl⁻, (a2-d2) FeO₂, (a3-d3) FeO₂H⁻, (a4-d4) FeOCl⁻, (a5-d5) Fe₂, and (a6-d6) CFe⁻ secondary ions for 1018 mild steel (a) before and (b-d) after immersion in 1 wt% NaCl solution saturated with CO₂ for different times: (b) 3min, (c) 10 min, and (d) 1 h (burst alignment mode; analyzed area: 100 μ m × 100 μ m; sputtered area: 300 μ m × 300 μ m).

The CFe⁻ ion signal represents the cementite phase (Fe₃C) in the steel substrate. No correlation of Fe₃C with the distribution of iron hydroxide or iron chloride intermediates is observed.

These experiments were all conducted in stagnant solutions. Even if all of the previous electrochemical tests have indicated that flow does not influence the anodic dissolution of iron, in the future it could be interesting to use ToF-SIMS to see if there are any effects of flow on adsorbed intermediates, particularly the role and distribution of chloride.

3.2 | Further Time-of-Flight-Secondary Ion Mass Spectroscopy Analysis of the Role of CO_2 in Iron Dissolution Reaction

From the results and discussion presented above, it appears that ToF-SIMS results are consistent with the notion that the iron dissolution reaction for mild steel in acidic media containing chloride ions seems to proceed according to four parallel dissolution paths, details of which described in Part I of this article series.¹³ This includes the formation of various hydroxide intermediates (in the first three dissolution paths) and chloride intermediates (in the fourth dissolution path). However, the presence of carbonic species in the intermediate complexes was not indicated by the EIS measurements, neither was it detected by the analytical methods used here, yet we know that there is an effect of aqueous CO_2 on the rate of anodic dissolution of iron. Hence, the exact role of CO_2 in the corrosion process still seems unclear.

To further explore the role of CO₂ in the iron dissolution reaction process, ToF-SIMS depth profiles and 3D image measurements were performed on the specimen immersed in NaCl solution (adjusted pH = 3.9), but this time saturated with Ar so that a comparison with the specimen immersed in the CO₂ saturated NaCl solution could be done. The results are shown in Figures 3 and 4. As seen in Figure 3, the FeO_2 depth profile for the 3 min of immersion in Ar saturated NaCl solution is similar to the FeO₂ depth profile for the native surface (Figure 1[a]) (peaks below 50 s of sputtering), and the behavior of the FeO₂⁻ signal after 10 min immersion is observed for 3 min immersion for CO₂ saturated NaCl solution (Figure 1[b]) (showing a slower intensity decrease after 20 s sputtering). One can draw a conclusion that the behavior observed after 3 min of immersion in CO2 saturated solution is delayed and observed only after 10 min in an Ar-saturated strong acid solution. This indicates that the steel was less rapidly corroded in the Ar saturated solution than in CO₂ saturated solution although the initial pH value for these two solutions was the same (pH 3.9). The Fe_2^- signal has an obvious intensity plateau starting at around 70 s of sputtering in Figure 3(c) which is different when compared to the specimen immersed in CO₂ saturated solution for 1 h that has no obvious intensity plateau (Figure 1[d]). Similarly, the Cl⁻ signal is also different from the saturated intensity observed in the CO₂ solution with 1 h immersion, while there is no saturated intensity observed in the probed thickness for 1 h immersion in strong acid solution

SCIENCE SECTION





FIGURE 3. ToF-SIMS negative ions in-depth profiles for 1018 mild steel (a-c) after immersion in 1 wt% NaCl solution (adjusted pH = 3.9 by adding HCl) saturated with Ar for different immersion times: (a) 3 min, (b) 10 min and (c) 1 h.

in Figure 3(c). Both behaviors of the Fe_2^- and Cl^- signals confirm that the specimen is less corroded in the Ar saturated solution than in CO_2 saturated solution at the same pH.

Meanwhile, the behavior of FeO₂H⁻ and FeOCl⁻ depth profiles are the same in the solutions with or without CO₂ at the same pH, indicating the mechanisms of iron dissolution are similar in these two solutions, i.e., that the oxide/hydroxide layer is transformed from mainly an iron oxide into a mixture of catalytic iron oxide/hydroxide and chloride intermediate containing layer. Based on the analysis of the FeO₂, Fe₂, and Cl⁻ depth profiles shown above, the only difference observed for these two solutions is that the specimen is less corroded in the solution without CO_2 (at the same pH), i.e., only the kinetics is modified. On the one hand, this is consistent with the "buffering effect" in the cathodic reaction: the dissolved CO₂ and H₂CO₃ in CO₂ saturated solution have buffering ability and can continuously provide extra protons, involved in the cathodic hydrogen evolution reaction.⁷⁻⁹ On the other hand, as for the anodic reaction, from the ToF-SIMS depth profile (Figure 1), no extra carbonate species signals were detected on the steel samples immersed in CO₂ solution, and similar trace amounts of carbonate species were observed for both CO₂ and the strong acid solution. Therefore, further investigation with ToF-SIMS

mappings was performed to explore the role of $\rm CO_2$ in anodic iron dissolution reaction.

Figure 4 shows the ToF-SIMS 3D chemical mappings of selected ions obtained on the specimens immersed in Ar-saturated NaCl solution for different immersion times. The selected Cl⁻, FeO₂, FeO₂H⁻, and FeOCl⁻ ions 3D chemical mappings are the integrated images for the oxide/hydroxide layer regions, corresponding to the depth profiles shown in Figure 3, over the first 50 s, 60 s, and 70 s of sputtering for 3 min, 10 min, and 1 h, respectively. The selected Fe₂ and CFe⁻ 3D images are the integrated images of the steel substrate regions after the sputtering of the oxide/hydroxide layer.

Looking at FeOCI⁻ ions in Figures 4(a4) through (c4), an obvious difference with CO₂ saturated solution is that the intensity of FeOCI⁻ ions on the surface is much lower in strong acid solution without CO₂ for the same immersion time. Especially at short immersion times (3 min and 10 min), there are no detectable aggregates of iron chloride intermediates, and also no "defects" or "pits" on iron oxides (FeO₂), iron hydroxides (FeO₂H⁻), and substrate (Fe₂). Similar observation was made for chloride ions mappings in Figures 4(a1) through (c1). The "pits" on the substrate (Fe₂), which are caused by the localized chloride reaction with the iron substrate, start to show up only at 1 h

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FIGURE 4. ToF-SIMS 3D negative ions chemical maps of (a1-c1) Cl⁻, (a2-c2) $FeO_{2'}$ (a3-c3) FeO_2H^- , (a4-c4) $FeOCl^-$, (a5-c5) Fe_2^- , and (a6-c6) CFe^- secondary ions for 1018 mild steel (a-c) after immersion in 1 wt% NaCl solution (pH = 3.9) saturated with Ar for different times: (a) 3 min, (b) 10 min, and (c) 1 h (burst alignment mode; analyzed area [i.e., size image]: 100 µm × 100 µm; sputtered area: 300 µm × 300 µm). The intensity range for each ion is the same as in Figure 2 (CO₂ solution).

immersion in strong acid solution, while in CO₂ solution the "pits" formed at 3 min immersion and at 1 h the chlorides reaction intermediates not only formed locally but have already spread over the whole surface area. This indicates that the adsorption of chloride ions and formation of the chloride-containing complexes is faster in CO₂ saturated solution than in strong acid solution without CO₂. This observation indicates that CO₂ might influence the iron dissolution kinetics by the acceleration of chloride ions adsorption and iron chloride intermediates formation. However, the exact consequences of this observation on mechanisms of iron dissolution are still not elucidated. The link between CO₂ and the formation of chloride adsorbates is suggested by ToF-SIMS results and a more thorough investigation is required at different chloride concentrations to clarify this effect by using electrochemical measurements etc.

CONCLUSIONS

This study reports the investigation of the anodic iron dissolution mechanisms for mild steel corrosion in chloride-containing CO_2 environment.

➤ ToF-SIMS in-depth profiles and 3D images detect parallel formation of iron hydroxide and iron chloride intermediates on 1018 mild steel surfaces with the increase of immersion time at OCP.

➤ ToF-SIMS depth profiles indicate that there is no additional formation of iron carbonate species on 1018 mild steel or iron surface corroding in an aqueous CO_2 environment, which is consistent with the previous reports of Almeida, et al.,²³ and Moradighadi et al. in Part I of this article series.¹³ This indicates that carbonate species do not directly participate in the iron dissolution reaction by forming intermediate adsorbates in the same way as hydroxides and chlorides do.

> In the 1 wt% NaCl solution, at the initial stage of the corrosion process, the chloride reaction with mild steel is more localized with the formation of "pits" filled with iron chloride or oxychloride intermediates. At longer immersion times, with the development of general corrosion, the iron chloride intermediates spread all over the steel surface.

➤ The ToF-SIMS in-depth profiles confirmed that the iron dissolution kinetics is accelerated in the CO₂ environment compared to strong acids without CO₂ at the same pH. ToF-SIMS 3D mappings results with and without CO₂ further provided a basis for a hypothesis that the role of CO₂ could be to accelerate the adsorption of chloride ions and accelerate the formation of chloride intermediate adsorbates, thereby increasing dissolution kinetics of iron at the OCP. Further investigation is suggested to confirm the role of CO₂ and clarify the effect of chlorides in the iron dissolution process.

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